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Chemical Reactions of Chlorine on a Vicinal Si(100) Surface Studied by ESDIAD

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Abstract

The reaction of Cl_2 on a vicinal Si(100) surface has been studied by ESDIAD. This type of surface possesses two types of sites: pairs of dangling bonds on Si-Si terrace dimers, and single dangling bonds on the 2-atom layer high steps. The reactivity of these two sites is compared. For low coverages the step dangling bonds are identified as the preferred Cl bonding site after 673K-annealing. Upon higher temperature annealing and $SiCl_2(g)$ desorption, the terrace-site Cl species are depleted more rapidly than the step-site Cl species. Extensive isothermal etching under a continuous Cl_2 flux at 800K is found to produce a disordered surface structure. Heating to 1123K causes a reordering of the surface.

1. Introduction

Dry etching of silicon crystals by halogens is one of the most important processes in manufacturing of the very-large-scale integration (VLSI) devices. Chlorine, as the most commonly used halogen, has received particularly high attention in surface science studies [1-17]. In most of these studies, only the role of Si-Si terrace dimer sites on Si(100) is considered in the reaction mechanism [1- 5]. In reality, the Si(100) surface can not be ideally flat [18], and the terraces containing the Si-Si dimer sites are separated by steps possessing defective sites. The role of these defective step sites in the mechanism of dry halogen etching is not clear yet. The chlorine binding energy difference between terrace sites and step sites is very small, making their discrimination impossible for most of the surface sensitive analytical methods. Generally, only spectroscopies with a very high energy resolution (e.g. polarized infrared spectroscopy [19]), or the real space imaging techniques such as scanning tunneling microscopy (STM) [16], or electron stimulated desorption ion angular distribution (ESDIAD) [17] can be used to differentiate site specific chemistry.

Since the role of steps on Si(100) surfaces can be significant for dry etching reactions [16], a detailed understanding of step reconstruction and chemistry is needed. Different theoretical models of the step reconstruction on Si(100) surfaces have been developed [20, 21]. The STM studies by Griffith et al. [22] and our previous ESDIAD study of chlorine bonding on vicinal Si(100) [17] have confirmed the Chadi model of rebonded reconstruction of 2-atom layer height steps [20] as shown in Figure 1. Here, the only stable reconstruction of the 2-atom layer height steps is that with the Si-Si dimers oriented parallel on both upper and lower terraces.

Various surface sensitive techniques have been applied to obtain information about Cl_2 dissociative adsorption, Cl bonding, and the production of chlorine-containing etching products on Si(100) surfaces. The dissociative adsorption of Cl_2 was investigated using molecular beam scattering experiments [10]. The dependence of the initial Cl_2 sticking coefficient for low energy thermal Cl_2 beams on the Cl_2 translational energy and on the Si(100) crystal temperature were interpreted in terms of a precursor-mediated adsorption mechanism involving the existence of a transient Cl_2 physisorbed state. In addition, a metastable configuration of the Cl species, symmetrically bridge bonded to the Si-Si dimer, was recently postulated in combined ESDIAD/HREELS studies [6,7], and later independently confirmed in a STM study by Boland [8]. This metastable bridged Cl configuration is completely converted to terminally-bonded Cl upon annealing to 673K [6]. The terminal bonding of Cl species on the dangling bonds of the Si-Si dimers, as the minimum energy configuration, was confirmed by many surface sensitive techniques [1-9, 23].

Using the temperature programmed desorption (TPD) technique, the main desorption species from the chlorine overlayers were determined [7, 12, 13]. Two desorption features are observed, a $SiCl_4(g)$ desorption maximum around 450-500K, and a $SiCl_2(g)$ desorption maximum around 850-950K [7, 13]. The isothermal etching products were also identified using a molecular beam scattering experiment [14]. Above ~ 800K, $SiCl_2(g)$ desorption was observed, accompanied by a significant increase of SiCl(g) evolution above ~ 1050K. No clear evidence of etching is observed below 800K.

In a STM study of bromine etching of the Si(100) surface [15], regions of (3x1) reconstruction are observed to form at the etching temperatures of 850-900K. The process is explained by the formation of alternating rows of Si-Si dimers saturated by monobromide terminal species separated by rows of Si atoms bonded as dibromide species. Upon heating the $SiBr_2$ species desorb, preserving the rows of the Si-Si dimers spaced by rows of missing Si atoms on the surface. The first study dealing in detail not only with halogen-driven etching of the terrace Si-Si dimer sites but also with the etching of the step sites is the STM study by Chander et al. [16]. The preferential bromine etching at 900K of the S_B type of steps (adjacent to upper terrace containing Si-Si dimer bonds parallel to the step edge [20]) is observed. In comparison the etching of the terrace Si-Si dimer sites and S_A step sites (adjacent to upper terrace containing Si-Si dimer bonds perpendicular to the step edge [20]) is slower. A rough equilibrium surface structure involving three Si layers is achieved on the surface after long Br_2 exposures.

To study the reactivity of such sites, we have selected the vicinal Si(100) crystal (6° off-axis angle from the <100> direction towards the <011> direction) possessing predominantly 2-atom layer height steps designated D_B steps, as shown in Fig. 1. In this work we employ the digital ESDIAD technique to study reactivity of dangling bonds present on the D_B type steps with molecular chlorine. Using this type of crystal we can distinguish by ESDIAD between the adsorption on the step and terrace sites because of the difference in Si-Cl bond directions. The possible overlap of the Cl^+ ESDIAD beams from the steps and from the terraces with dimers oriented perpendicular to the steps (present on nominally flat Si(100) surfaces) is avoided in this way.

Upon low temperature adsorption of Cl_2 at 140K we observe bridge-bonded Cl species on the terrace Si-Si dimer sites and terminally-bonded Cl species on the 2-atom layer high step sites. The bridge-bonded Cl species on terraces are converted upon 673K heating to terminally-bonded Cl species in agreement with other studies [6, 7, 17]. Upon adsorption of low Cl coverages, and subsequent annealing to 673K, preferential Cl bonding on the step sites is observed. The Cl-saturated surface is etched upon annealing to 873K, and only the step-bonded Cl species are found to be preserved. Intensive isothermal etching at 800K produces a strong central Cl^+ emission which is explained by disordering of the surface.

2. Experimental

Details of the ultrahigh vacuum (UHV) system (base pressure $3x10^{-11}$ Torr) and the Si(100) sample preparation have been described previously [24]. The UHV system is equipped with a CMA Auger electron spectrometer (AES), an argon-ion sputtering gun, a digital LEED/ESDIAD apparatus, a shielded quadrupole mass spectrometer (QMS) for line-of-sight temperature programmed desorption (TPD) experiments, and an additional QMS coupled with an electron gun for ion mass analysis during electron stimulated desorption (ESD) processes. The vicinal Si(100) crystal ($12\times12\times1.4$ mm^3, 10 Ωcm, p-type, boron doped) was cut 6° off the <100> direction towards the <011> direction. The step orientation was checked with the Laue back-reflection X-ray diffraction technique. Cleaning of the crystal was performed by combined Ar^+ sputtering and subsequent annealing at 1200K. After the cleaning procedure the crystal was slowly cooled (~ 3 Ks^{-1}) to room temperature. This cooling procedure was employed during all experiments to obtain a well-ordered (2x1) LEED pattern indicating one domain terrace site structure. The concentration of carbon and oxygen impurities in the depth of Auger sampling was measured by AES before each experiment and was found to be below the detection level (< 1 atomic %). A multicapillary-collimated doser with an absolutely calibrated molecular flux and a known angular distribution was used for dosing Cl_2 (source: Matheson, 99.999%) [25]. The values of θ/θ_{sat} were determined from TPD areas of the dominant desorption product, $SiCl_2$. It was shown with an auxiliary quadrupole mass spectrometer (ion source turned off) that Cl^+ ions were dominant ions, produced by the ESD process on the Cl-covered crystal. All ESDIAD images were obtained at a crystal temperature of 140K using an electron energy of 120eV. The effect of the structureless background (mainly due to soft X-rays) is minimized by subtraction of the pattern obtained in the configuration where all positive ions are retarded in the ESDIAD analyzer. Small inhomogeneities in the response of the multichannel plate detector were removed by 5 point polynomial smoothing of the ESDIAD patterns [26].

3. Results and Discussion

The reconstruction of the D_B step in the step region of the vicinal Si(100) surface is shown by top, side and three-dimensional views in Fig. 1 (after Chadi [20]). It can be seen that this type of the reconstruction introduces a row of unpaired dangling bonds on the D_B step defective sites in addition to the terrace Si-Si dimer sites. The row of unpaired dangling bonds on the D_B step is structurally very similar to the row of unpaired dangling bonds on the S_B type of 1-atom layer height step, suggesting that similar behavior can occur for these two different steps. In this section we compare the reactivity of the terrace and the D_B step sites present on vicinal Si(100) using the ESDIAD technique.

3.1. Thermal Development of Cl^+ ESDIAD Pattern

The development of Cl^+ ESDIAD pattern as a function of annealing temperature is shown in Fig. 2. All images are obtained at 140K with the crystal biased to +8V. Each pattern is shown as a three-dimensional contour plot (top part of the figure) and a two-dimensional contour plot (bottom part of the figure). The three-dimensional plots have the same vertical scaling with equidistantly stepped contours to show the relative height of the ESDIAD features. The two-dimensional contour plots are presented with six contours equidistantly spaced from zero to maximum intensity. All ESDIAD images presented in following figures are obtained under the same conditions and are drawn in the same way as in Fig. 2.

Upon adsorption at 140K (see Fig. 2a) two Cl^+ beams are observed, the stronger Cl^+ emission in the <100> terrace normal direction, and the weaker off normal Cl^+ emission in the <011> downstairs step direction. The <100> terrace normal emission was first observed in our flat Si(100) surface studies [6, 7] and was assigned to the bridge-bonded Cl species on Si-Si terrace dimers, based on the normal direction of Cl^+ ESDIAD beam emission and also on the observation of a 295 cm^{-1} vibrational mode characteristic for bridging Cl. The origin of the downstairs-oriented step Cl^+ emission was discussed in detail in our previous study of chlorine bonding on the vicinal Si(100) surface [17], and was interpreted as Cl^+ emission from the step defect sites shown in Fig. 1. On the silicon terrace dimer sites the transformation of the metastable bridge-bonded Cl to the terminally-bonded Cl upon annealing to 423 and 673K is accompanied by an increase of the Cl^+ yield as shown in Fig. 2b and 2c, respectively. The same type of transformation was also observed on the flat Si(100) surface [6, 7]. No change of the direction for the Cl^+ step emission occurs. Only a very small amount of desorbing $SiCl_4(g)$ is observed in this temperature range, compared to the main desorption of $SiCl_2(g)$ at ~ 840K [7], suggesting that the observed changes (from Fig 2a to 2c) occur without significant change of the surface Cl coverage. Despite the fact that the number of surface Cl atoms adsorbed on steps can be only 1/7 to 1/8 of that on the terraces at full coverage, the Cl^+ step emission is more intense than the Cl^+ terrace emission. This can be explained by a lower reneutralization rate for the step Cl^+ ions due to their larger distance from neighboring Cl atoms on the same row and on the lower terrace, compared to Cl on terrace dimer sites.

Subsequent changes of the ESDIAD pattern upon annealing to 823K and 873K are shown in Fig. 2d and 2e, respectively. In this region of temperatures, the significant desorption of $SiCl_2(g)$ occurs as observed in TPD spectra [7]. The most significant change in pattern 2d is the strong increase of the terrace Cl^+ emission. To explain this effect, the dependence of the Cl^+ yield from the terraces on the Cl coverage has to be considered. An increase of the Cl^+ yield for increasing Cl coverages in the range $\theta/\theta_{sat} < 0.5$, and subsequent decrease of the Cl^+ yield for increasing Cl coverages in the range $\theta/\theta_{sat} > 0.5$ was found on flat Si(100) [7]. The decrease of the Cl^+ yield is explained by quenching of Cl^+ ions by neighboring Cl atoms for higher Cl coverages [7]. Thus upon desorption of $SiCl_2(g)$, the decrease of overall Cl surface concentration lowers the Cl^+ quenching rate, and increases the terrace Cl^+ yield. An increase of the step Cl^+ emission also occurs, and is attributed to reduction of a similar quenching effect by loss of $SiCl_2$. The smaller relative increase of the step Cl^+ intensity compared to the increase of terrace Cl^+ intensity again indicates the smaller effect of the quenching of excited surface species produced by electron stimulated desorption (ESD) on the steps.

A very interesting observation is evident after annealing to 873K following additional desorption of $SiCl_2(g)$ (see Fig. 2e). The Cl^+ emission preferentially disappeared from the terrace sites preserving Cl^+ emission from the step sites. Two different $SiCl_2(g)$ desorption mechanisms may be postulated to explain this effect: (1) the etching reaction to produce $SiCl_2(g)$ occurs preferentially on the step sites with fast diffusion of the Cl atoms from the terrace sites, refilling new unsaturated dangling bonds on the step sites; (2) the preferential etching reaction occurs on the terrace sites at lower desorption temperatures with the preservation of Si-Cl bonds on the steps followed by step-$SiCl_2$ desorption at higher desorption temperatures. We are not able to determine which is the correct mechanism at present. Based on the STM study by Chander [15] of preferential Br_2 etching of the S_B steps and structural similarities of S_B and D_B steps we favor mechanism (1) involving preferential step etching followed by Cl migration to new step sites produced by etching.

3.2. Preferential Step Bonding

As mentioned in section 3.1. the Cl^+ ESD yield does not increase linearly with the Cl coverage. This complicates an ESDIAD analysis designed to determine whether there is preferential bonding of Cl on the step or terrace sites. We overcame this problem using only very low Cl coverages ($\theta/\theta_{sat} < 0.2$) for an ESDIAD measurement of the development of Cl^+ peak intensities. In this low Cl coverage range we assume that effect of quenching by neighboring Cl atoms is negligible. The correctness of this assumption is supported by the observation of a linear increase of Cl^+ yield observed for the terminal Cl species on the terraces of the flat Si(100) surface in this range of Cl coverage [7].

The result of our analysis is shown in Figure 3. The ESDIAD patterns used for the analysis in this figure were obtained after low temperature adsorption of Cl_2 molecules and subsequent annealing to 673K to convert the terrace-bridge bonded-Cl species to the terminally-bonded species. The relative Cl coverage scale was obtained from the yield of $SiCl_2(g)$ observed by TPD (desorption at ~ 840K) for different Cl_2 exposures. The contribution of $SiCl_4(g)$ desorption (desorption at ~ 500K) represents less than 3% of area of the $SiCl_2$ desorption peak and is neglected. The curves marked by empty and filled triangles represent the dependence of the ESDIAD Cl^+ emission intensity, at the maxima, as a function of total Cl coverage. The Cl^+ emission intensities from the steps (S) (empty triangles) and the terraces (T) (filled triangles) are shown in Fig. 3 as well as the ratio S/T. The drop of the S/T ratio with increasing coverage indicates the preferential population of the step sites with respect to the terrace sites at lower coverages. Two possible reasons for this effect may be considered: (1) a lower sticking coefficient on the terrace sites during Cl_2 adsorption at 140K, and/or (2) migration of Cl atoms from the terraces to the steps during 673K annealing. No matter which kinetic process is kinetically controlling the site selection, Fig. 3 clearly shows that after annealing at 673K the dangling bonds present on the steps are preferentially populated. It should be noted that the S/T ratio would move in the opposite direction with coverage if the effect shown in Fig. 3 is influenced by enhanced ESD quenching of Cl^+ ion production on terrace sites as the Cl coverage is increased.

3.3. Surface Etching

We present two different experiments, employing ESDIAD to study the surface structure after performing the reaction with Cl_2 to an increasing extent of Si etching. In these experiments we use Cl_2 gas, not only as an etching gas, but for the production of an ESDIAD image to observe the orderliness of the vicinal Si(100) surface.

The first approach is shown in Fig. 4. The ESDIAD images are shown during two subsequent cycles of Cl_2 saturation adsorption (at 673K) followed by $SiCl_2$ desorption (at 873K). In addition the effect of final adsorption of Cl_2 at 673K is shown in Fig. 4c. During the desorption (etching) part of the cycle, the temperature is linearly increased to 873K with a heating rate of ~ 3K/s. Extensive etching of ~ 0.7 monolayer (ML) of Si atoms is produced by this two-cycle procedure. The amount of etched Si is calculated using an estimated upper limit saturation coverage of 0.7 Cl/Si on Si(100) [7] and the measured area of the $SiCl_2$ TPD desorption peak from the vicinal Si(100) surface. The Cl readsorbed at 673K on such a prepared surface (Fig. 4c) followed by an ESDIAD measurement serves as a qualitative method for imaging of the disorder of the surface. It is seen from a comparison of Fig. 4a and 4c, that within our ESDIAD resolution, the etching of ~ 0.7 ML of Si does not change the distribution of the Cl^+ ESDIAD ejection directions suggesting a very similar surface structure following this amount of Si removal.

Figure 5 shows the isothermal etching by Cl_2 at a lower temperature (800K). After a certain etching time the temperature is lowered to 673K and the surface is resaturated with chlorine for the ESDIAD imaging. Negligible etching occurs upon Cl_2 readsorption at 673K [7, 14] and we do not add it to the estimate of the amount of etched Si. The degree of etching is obtained using a comparison of the mass spectroscopic measurement of the isothermal $SiCl_2(g)$ desorption (measured at m/e = 63^+, $SiCl^+$) at 800K from the chlorine saturated surface with the Cl_2 beam <u>off</u> (saturation 0.7 Cl/Si gives 0.35ML of desorbing $SiCl_2$) with the area of the desorbing $SiCl_2$ obtained with the Cl_2 beam <u>on</u>. After resaturation at 673K the beam of Cl_2 is shut off, the crystal is cooled to 140K, and the ESDIAD image is taken. This procedure is repeated several times to map the surface structure transformations for a large range of etching activity. The temperature and Cl_2 flux cycle is shown in the bottom part of Fig. 5. The resulting ESDIAD images during the etching of several monolayers of Si are shown in the top part of the Fig. 5. The development of the strong central beam in the terrace normal <100> direction during Cl_2 etching of ~ 0.7, 2.6, and 4.4 ML of Si at 800 K is shown in Figures 5b, 5c, and, 5d, respectively. The reordering to the original surface morphology (as judged by ESDIAD) after 3 minutes of high temperature annealing at 1123K is shown in figure 5e.

We attribute the strong central Cl^+ beam to the disordering of the surface by etching. This ESDIAD pattern indicates the superposition of random Si-Cl bond directions and/or of the bending of the Cl^+ trajectories towards the surface normal direction by the image potential gradient on the dense steps [27], caused by extensive surface disordering. The other possibility which has to be considered is the possible presence of isolated Si atoms with normally oriented dangling bonds, produced by extensive etching. It was shown in the low-energy electron energy loss spectroscopy (LEELS) study by Aoto et al. [11] that the LEELS features of Cl on Si(100) are significantly changed after Cl_2 etching in the temperature range of 800-1090K and resemble features observed after Si(111) (7x7) surface etching. Also in the STM study by Chander et al. [15], a change of the Si(100) (2x1) surface reconstruction is observed upon Br_2 etching at 850K. The removal of the rows of Si atoms from Si-Si dimers is observed, producing regions of (3x1) reconstruction resulting from the repeating pattern of the Si-Si dimer rows spaced by the rows of missing Si atoms.

This analysis shows that much deeper understanding is required to explain the mechanism of the Cl_2 surface etching reaction for different Cl_2 fluxes and various temperatures. From the comparison of etched surfaces in Fig. 4c (crystal temperature up to 873K, Cl_2 beam off during etching) and 5b (crystal temperature 800K, Cl_2 beam on during etching), we can conclude that these two modes of etching produce different morphology on the surface. Two factors have to be considered for explaining this difference: (1) the crystal temperature; and (2) the presence of the Cl_2 flux during etching. During the adsorption - desorption sequence (Fig. 4) the temperature is increased to 873K in comparison with 800K for the isothermal etching experiment (Fig. 5), allowing faster diffusion of Si surface atoms and more effective recovery of the ideal surface structure after etching. On the other hand, the constant Cl_2 flux employed in Fig. 5 could lead to the saturation of the step $SiCl_2$ desorption channel and the opening of the competitive desorption channel from the terrace sites causing more randomization during isothermal etching as observed in Fig. 5b.

4. Conclusions

Using the bond directional imaging capability of the ESDIAD technique we have compared the relative reactivity of chlorine gas on 2-atom layer height step sites and terrace Si-Si dimer sites present on a vicinal Si(100) surface. We conclude the following:

1. The dangling bonds present on the steps represent preferential bonding sites for Cl atoms at 673K, compared to the dangling bonds at Si-Si dimer sites on the terraces.

2. Annealing of the crystal to the temperature range of $SiCl_2$ desorption (~ 800K or higher) first depopulates Cl from the terrace sites and subsequently Cl from the step sites.

3. Fractional monolayer desorption of $SiCl_2$ at 873K leads to the production of a surface with dangling bond orientations identical to those of the unetched surface.

4. Multilayer desorption of $SiCl_2$ at 800K under constant Cl_2 flux leads to the production of a disordered surface where chemisorption directions of Cl on the step and terrace sites can not be resolved by ESDIAD.

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Figure Captions

Fig. 1: Schematic side, top, and 3-D views of the vicinal Si(100) surface with structure proposed by Chadi [20]. Reactive sites in the side and top views are shown as white circles with the specified directions of the dangling bonds shown schematically by a half filled orbital. Four coordinated bulk Si atoms are shown as filled circles. The size of the circles characterizes the height of silicon atoms along the [100] axis.

Fig. 2: The Cl^+ ESDIAD pattern evolution as a function of annealing temperature for saturation chlorine adsorption on vicinal Si(100) measured at 140K under the following conditions: electron beam energy E_e = 120eV; crystal current I_e = 4nA; crystal bias V_b = +8V.

Fig. 3: The dependence of Cl^+ ESDIAD beam intensity (peak maximum) for the step site emission (S) (empty triangles) and the terrace site emission (T) (filled triangles) on the relative Cl coverage, θ/θ_{sat}. The resulting S/T ratio is shown by filled circles.

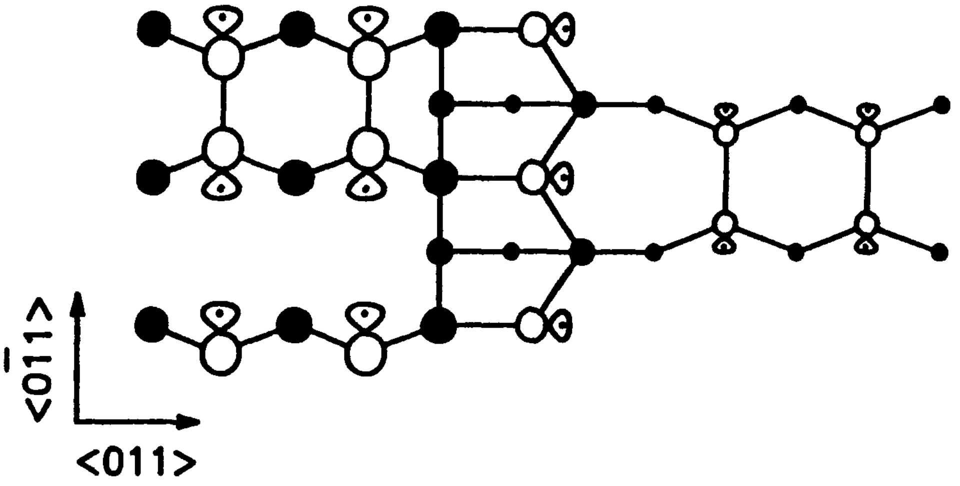
Fig. 4: The evolution of Cl^+ ESDIAD patterns during two cycles of Cl_2 adsorption and $SiCl_2$ desorption (a and b), followed by Cl_2 readsorption (c). Images are obtained under the same conditions as in Fig. 2.

Fig. 5: Chlorine etching of vicinal Si(100) monitored by Cl^+ ESDIAD imaging. The Cl^+ ESDIAD images are obtained at 140K following saturation Cl_2 adsorption at 673K. (a) initial Cl saturated surface, (b), (c), (d) surface after etching of 0.7, 2.6, and 4.4ML of Si, respectively, (e) surface annealed for 3 minutes at 1123K.

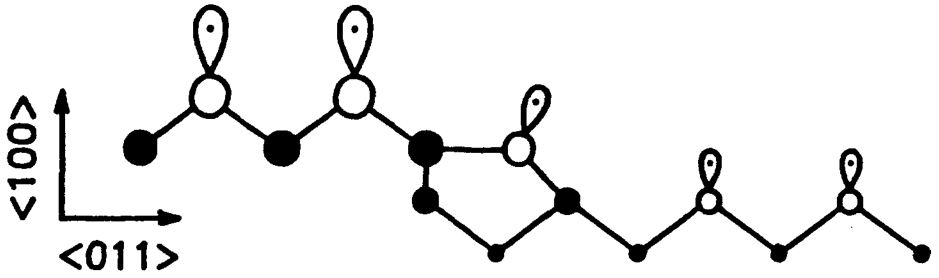
ESDIAD images are obtained under the same conditions as in Fig. 2. The temperature and Cl_2 flux schedules are shown at the bottom.

Model of Surface Structure of Diatomic Steps on Vicinal Si(100) Surface (after Chadi)

Top View



Side View



3 Dimensional View

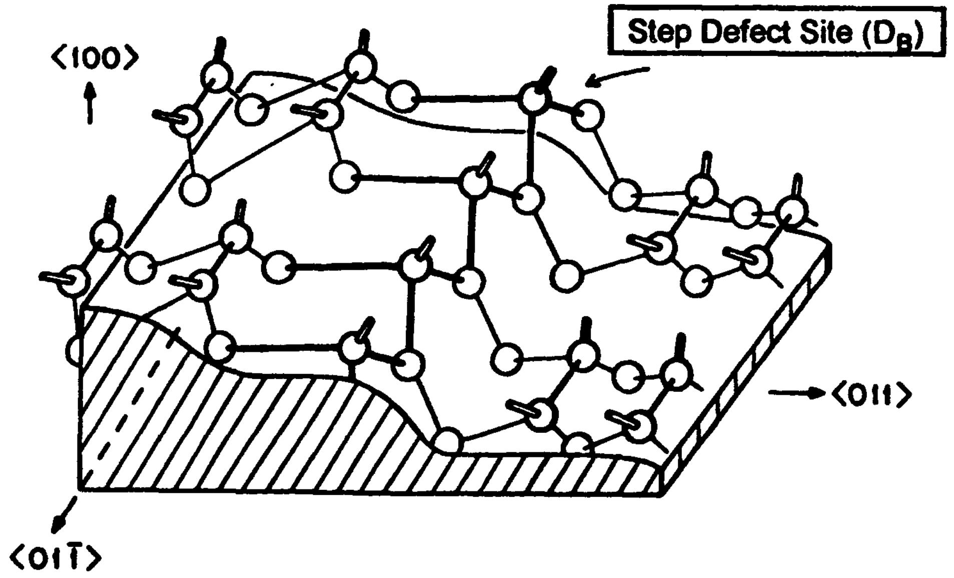


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Figure 1

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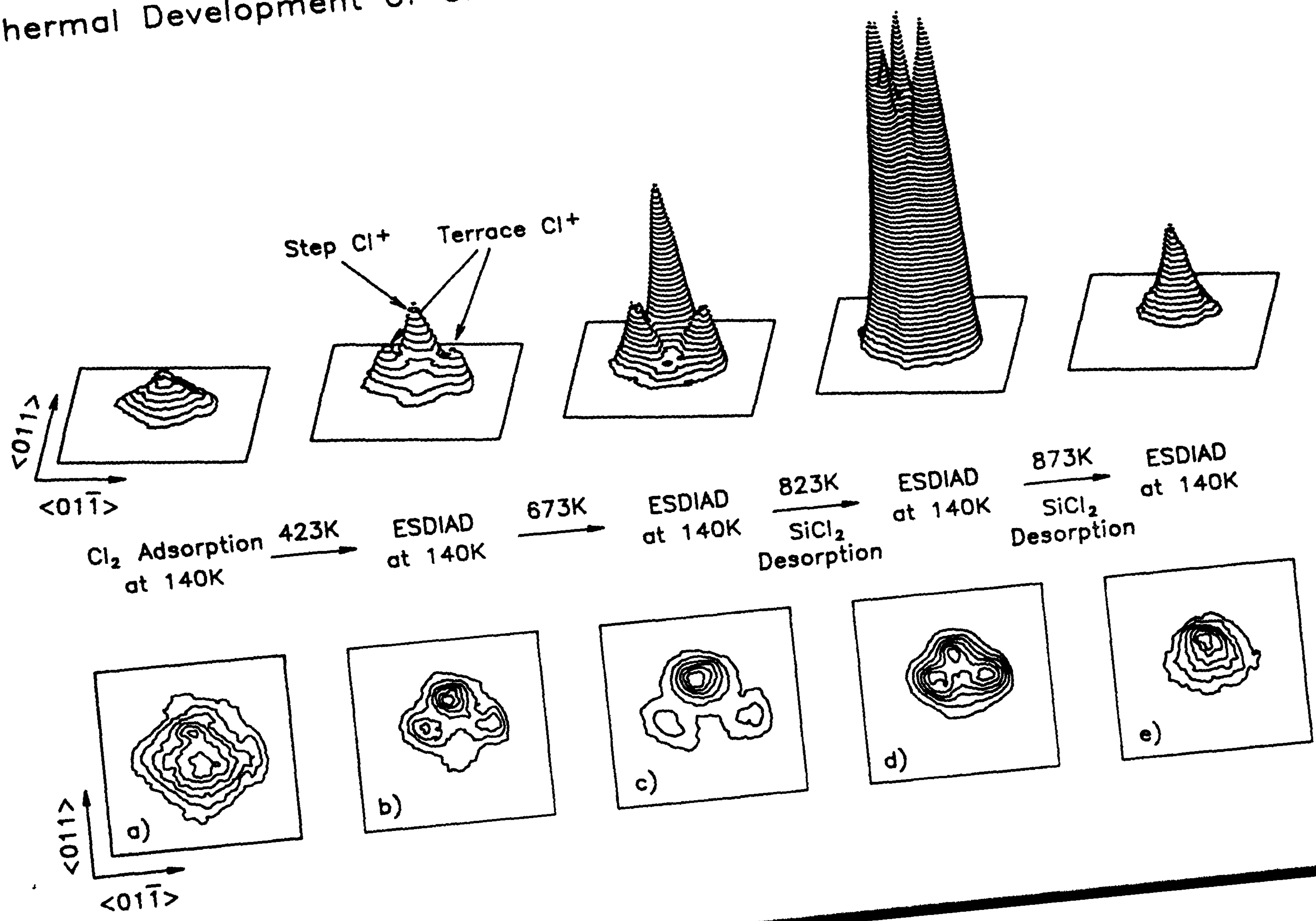
Figure 2

Thermal Development of Cl^+ ESDIAD Pattern for Cl on Vicinal Si(100)



Relative Population of Step And Terrace Sites as A Function of Cl Coverage on Vicinal Si(100)

(Low Coverage range)

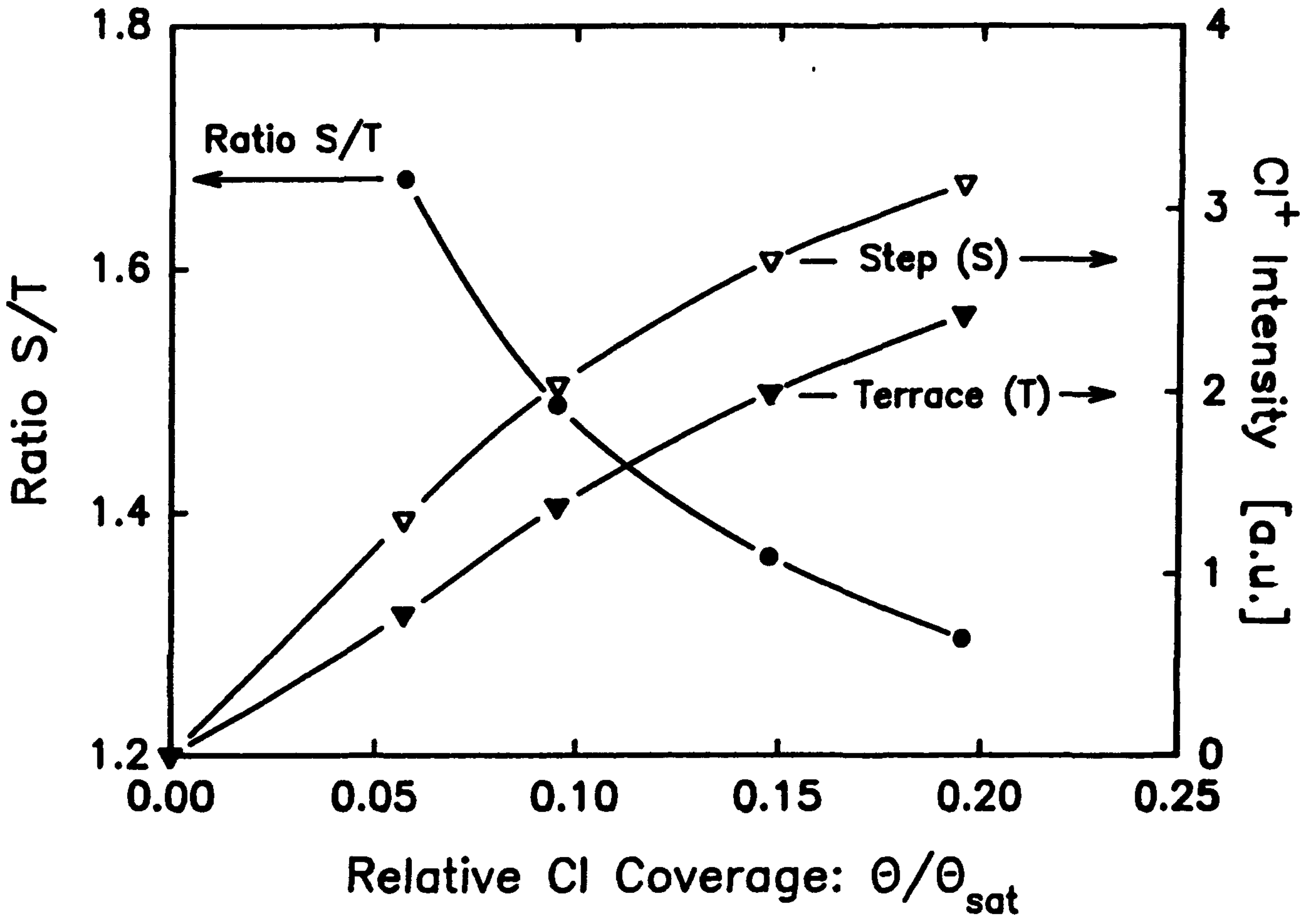


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Figure 3

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Figure 4

Cl$^+$ ESDIAD Sequence of
Two Cl$_2$ Saturation Adsorption – Desorption Cycles

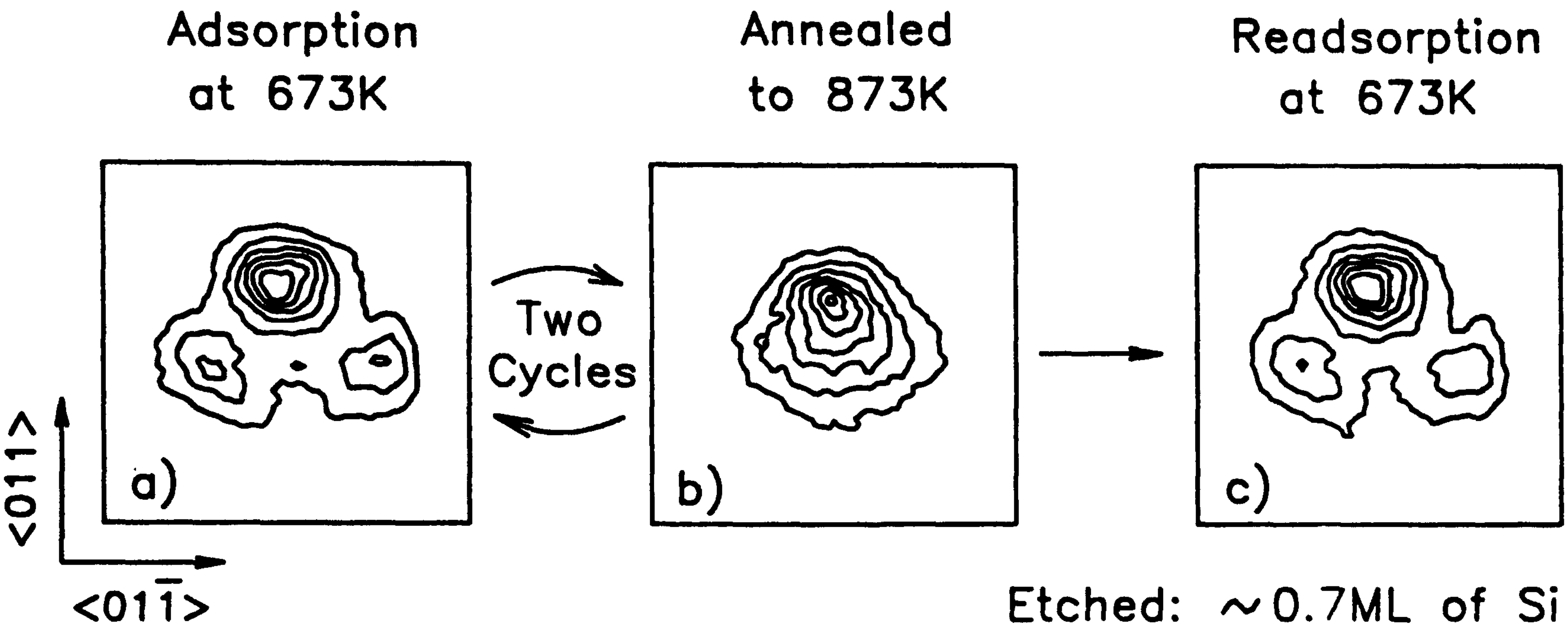

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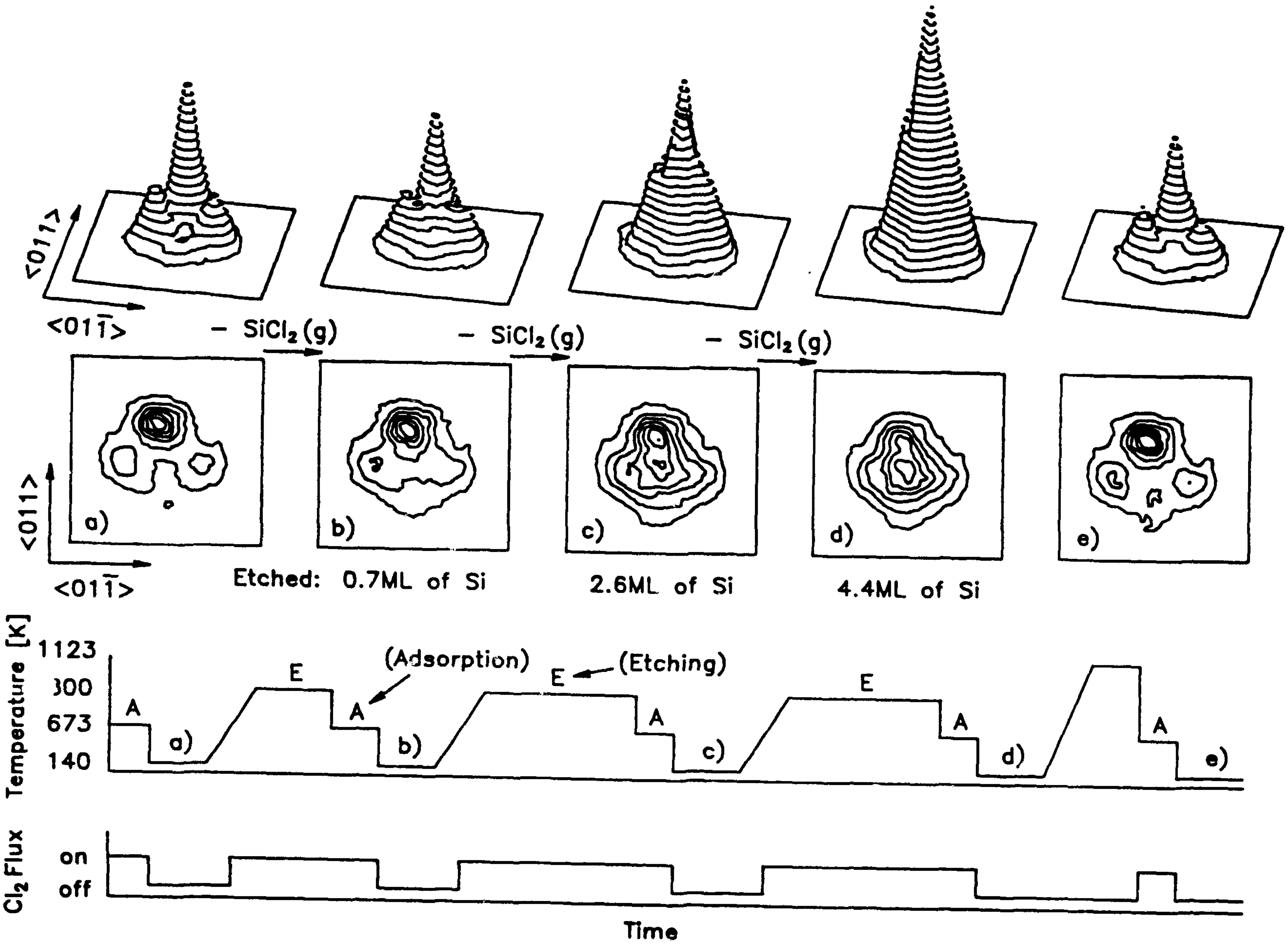
Figure 5

Chlorine Etching of Vicinal Si(100) monitored by Cl$^+$ ESDIAD Imaging
(Patterns Following Cl$_2$ Readsorption at 673K)



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